

## THE CLAIMS

### What is claimed is:

1. A process for forming a nitride material on a substrate, including the steps of volatilizing a nitrogen-containing precursor to form a corresponding precursor vapor, and contacting the substrate with the precursor vapor under chemical vapor deposition conditions to deposit said nitride material, wherein said precursor comprises a compound of formula (I):



wherein:

M is selected from the group of Ta, Ti, W, Nb, Si, Al and B;

a is a number equal to the valence of M;

$1 \leq b \leq (a-1)$ ;

$R_1$  and  $R_2$  can be the same as or different from one another, and are each independently selected from the group of H, C<sub>1</sub>-C<sub>4</sub> alkyl, C<sub>3</sub>-C<sub>6</sub> cycloalkyl, and R<sup>0</sup><sub>3</sub>Si, where each R<sup>0</sup> can be the same or different and each R<sup>0</sup> is independently selected from H and C<sub>1</sub>-C<sub>4</sub> alkyl; and

X is selected from the group of chlorine, fluorine, bromine and iodine.

2. The process of claim 1, wherein M is selected from the group consisting of Ta and Ti.

3. The process of claim 1, wherein M is Ta.

4. The process of claim 1, wherein M is Ti.

5. The process of claim 1, wherein said contacting is carried out to adsorb precursor on the substrate as a first step, and a co-reactant nitrogen source that is reactive with the adsorbed precursor to form said nitride material, is contacted with the adsorbed precursor under reaction conditions for forming said nitride material, as a second step.

6. The process of claim 5, wherein the first and second steps are carried out alternatingly and repetitively with respect to one another, for sufficient number of repetitions to form said nitride material at a predetermined thickness.

7. The process of claim 6, wherein said predetermined thickness is in a range of from about 1 to about 100 nanometers.

8. The process of claim 5, wherein said co-reactant nitrogen source is selected from the group consisting of ammonia, alkyl amines, boranes, borazines, hydrazine, dialkyl hydrazine and tetraalkyl hydrazine.

9. The process of claim 5, further comprising between said first and second steps an intervening step of contacting the substrate with a purge gas to purge the substrate of first step gases prior to commencement of the second step.

10. The process of claim 9, wherein said purge gas comprises a gas selected from the group consisting of argon, nitrogen, helium,  $N_2O$ , hydrogen, and compatible combinations of two or more of the foregoing gases.

11. The process of claim 1, wherein said precursor further comprises a silicon source reagent, whereby said nitride material further comprises silicon therein.

12. The process of claim 11, wherein said silicon source reagent comprises a silane reagent selected from the group consisting of silane, alkylsilanes, halosilanes, and alkylhalosilanes, wherein alkyl is  $C_1$ - $C_4$  alkyl and halo is Cl, Br, F or I.

13. The process of claim 1, wherein said precursor further comprises an aluminum source reagent, whereby said nitride material further comprises aluminum therein.

14. The process of claim 13, wherein said aluminum source reagent comprises an alane reagent selected from the group consisting of alane, alkylalanes, haloalanes and alkylhaloalanes, wherein alkyl is C<sub>1</sub>-C<sub>4</sub> alkyl and halo is Cl, Br, F or I.

15. The process of claim 1, wherein said precursor comprises a boron source.

16. The process of claim 1, wherein said precursor comprises a boron precursor selected from the group consisting of borane, decaborane, alkylboranes and amidoboranes.

17. The process of claim 5, wherein one of said first and second steps is carried out in a pulsed manner relative to the other step.

18. The process of claim 1, wherein the contacting in a latter portion thereof comprises adding further source reagent to said compound of formula (I) to constitute said precursor, wherein said further source reagent comprises at least one reagent selected from the group consisting of silicon source reagents and aluminum source reagents.

19. The process of claim 1, wherein said precursor comprises a compound selected from the group consisting of:

(EtHN)<sub>6-b</sub>WX<sub>b</sub> wherein b is from 1 to 2 inclusive;

(EtMeN)<sub>6-b</sub>WX<sub>b</sub> wherein b is from 1 to 2 inclusive;

(Me<sub>2</sub>N)<sub>6-b</sub>WX<sub>b</sub> wherein b is from 1 to 2 inclusive;

(Et<sub>2</sub>N)<sub>6-b</sub>WX<sub>b</sub> wherein b is from 1 to 2 inclusive;

(EtHN)<sub>5-b</sub>MX<sub>b</sub> wherein M is Ta or Nb, and b is 1 or 2;

(EtMeN)<sub>5-b</sub>MX<sub>b</sub> wherein M is Ta or Nb, and b is 1 or 2;

$(\text{Me}_2\text{N})_{5-b}\text{MX}_b$  wherein M is Ta or Nb, and b is 1 or 2;  
 $(\text{Et}_2\text{N})_{5-b}\text{MX}_b$  wherein M is Ta or Nb, and b is 1 or 2;  
 $(\text{EtHN})_{4-b}\text{TiX}_b$  wherein b is from 1 to 2 inclusive;  
 $(\text{EtMeN})_{4-b}\text{TiX}_b$  wherein b is from 1 to 2 inclusive;  
 $(\text{Me}_2\text{N})_{4-b}\text{TiX}_b$  wherein b is from 1 to 2 inclusive;  
 $(\text{Et}_2\text{N})_{4-b}\text{TiX}_b$  wherein b is from 1 to 2 inclusive;  
 $(\text{EtHN})_{4-b}\text{SiX}_b$  wherein b is from 1 to 2 inclusive;  
 $(\text{EtMeN})_{4-b}\text{SiX}_b$  wherein b is from 1 to 2 inclusive;  
 $(\text{Me}_2\text{N})_{4-b}\text{SiX}_b$  wherein b is from 1 to 2 inclusive;  
 $(\text{Et}_2\text{N})_{4-b}\text{SiX}_b$  wherein b is from 1 to 2 inclusive;  
 $(\text{Me}_2\text{N})_{3-b}(\text{X})_b\text{Si-Si}(\text{X})_b(\text{NMe}_2)_{3-b}$  wherein b is 1 or 2;  
 $(\text{Et}_2\text{N})_{3-b}(\text{X})_b\text{Si-Si}(\text{X})_b(\text{NEt}_2)_{3-b}$  wherein b is 1 or 2;  
 $[(\text{Me}_3\text{Si})_2\text{N}]_{4-b}\text{TiX}_b$  wherein b is 1 or 2, and X is Cl, Br, F or I;  
 $[(\text{Me}_3\text{Si})_2\text{N}]_{5-b}\text{MX}_b$  wherein b is 2 or 3, X is Cl, Br, F or I, and M is Ta or Nb; and  
 $[(\text{Me}_3\text{Si})_2\text{N}]_{6-b}\text{WX}_b$  wherein b is 1 or 2, and X is Cl, Br, F or I.

20. The process of claim 1, wherein said precursor comprises silicon.

21. The process of claim 20, wherein said precursor comprises a compound selected from the group consisting of:

$[(\text{Me}_3\text{Si})_2\text{N}]_{4-b}\text{TiX}_b$  wherein b is 1 or 2, and X is Cl, Br, F or I;  
 $[(\text{Me}_3\text{Si})_2\text{N}]_{5-b}\text{MX}_b$  wherein b is 2 or 3, X is Cl, Br, F or I, and M is Ta or Nb; and  
 $[(\text{Me}_3\text{Si})_2\text{N}]_{6-b}\text{WX}_b$  wherein b is 1 or 2, and X is Cl, Br, F or I.

22. A process for forming  $\text{Si}_3\text{N}_4$  material on a nitrogen-functionalized substrate, comprising volatilizing a silicon-containing precursor to form a corresponding precursor vapor, and contacting the substrate with the precursor vapor under chemical vapor deposition conditions to deposit silicon material thereon, wherein said precursor comprises a compound of formula (II):



wherein:

X is Cl or Br;

m, n and y can each be the same as or different from each other, and each is independently from 0 to 3 inclusive; and

R and R' are the same as or different from one another, and each is independently selected from the group of H, C<sub>1</sub>-C<sub>4</sub> alkyl, and C<sub>3</sub>-C<sub>6</sub> cycloalkyl.

23. The process of claim 22, wherein said nitrogen-functionalized substrate comprises a surface functionalized with =NH and/or -NH<sub>2</sub> functionality.

24. The process of claim 22, wherein said compound of formula (II) is selected from the group consisting of:

ClSiH<sub>3</sub>;

H<sub>2</sub>SiCl<sub>2</sub>;

Me<sub>3</sub>SiCl; and

t-Bu<sub>2</sub>SiCl<sub>2</sub>.

25. The process of claim 22, wherein said nitrogen-functionalized substrate comprises an aminated substrate.

26. The process of claim 22, wherein said chemical vapor deposition comprises ALCVD.

27. The process of claim 22, wherein said nitrogen-functionalized substrate comprises a dielectric surface.

28. The process of claim 22, wherein said nitrogen-functionalized substrate comprises a low k surface.

29. The process of claim 1, wherein said nitride material comprises a migration barrier on said substrate.

30. The process of claim 29, wherein said nitride material comprises titanium nitride having a thickness in a range of from about 1 to about 100 nanometers.

31. The process of claim 29, wherein said nitride material comprises titanium silicon nitride.

32. A metalorganic precursor of formula (I):



wherein:

M is selected from the group of Ta, Ti, W, Nb, Si, Al and B;

a is a number equal to the valence of M;

$1 \leq b \leq (a-1)$ ;

$R_1$  and  $R_2$  can be the same as or different from one another, and are each independently selected from the group of H,  $C_1$ - $C_4$  alkyl,  $C_3$ - $C_6$  cycloalkyl, and  $R^0_3Si$ , where each  $R^0$  can be the same or different and each  $R^0$  is independently selected from H and  $C_1$ - $C_4$  alkyl; and

X is selected from the group of chlorine, fluorine, bromine and iodine.

33. The metalorganic precursor of claim 32, wherein M is selected from the group consisting of Ta and Ti.

34. The metalorganic precursor of claim 32, wherein M is Ta.

35. The metalorganic precursor of claim 32, wherein M is Ti.

36. The metalorganic precursor of claim 32, selected from the group consisting of:

- (EtHN)<sub>6-b</sub>WX<sub>b</sub> wherein b is from 1 to 2 inclusive;
- (EtMeN)<sub>6-b</sub>WX<sub>b</sub> wherein b is from 1 to 2 inclusive;
- (Me<sub>2</sub>N)<sub>6-b</sub>WX<sub>b</sub> wherein b is from 1 to 2 inclusive;
- (Et<sub>2</sub>N)<sub>6-b</sub>WX<sub>b</sub> wherein b is from 1 to 2 inclusive;
- (EtHN)<sub>5-b</sub>MX<sub>b</sub> wherein M is Ta or Nb, and b is 1 or 2;
- (EtMeN)<sub>5-b</sub>MX<sub>b</sub> wherein M is Ta or Nb, and b is 1 or 2;
- (Me<sub>2</sub>N)<sub>5-b</sub>MX<sub>b</sub> wherein M is Ta or Nb, and b is 1 or 2;
- (Et<sub>2</sub>N)<sub>5-b</sub>MX<sub>b</sub> wherein M is Ta or Nb, and b is 1 or 2;
- (EtHN)<sub>4-b</sub>TiX<sub>b</sub> wherein b is from 1 to 2 inclusive;
- (EtMeN)<sub>4-b</sub>TiX<sub>b</sub> wherein b is from 1 to 2 inclusive;
- (Me<sub>2</sub>N)<sub>4-b</sub>TiX<sub>b</sub> wherein b is from 1 to 2 inclusive;
- (Et<sub>2</sub>N)<sub>4-b</sub>TiX<sub>b</sub> wherein b is from 1 to 2 inclusive;
- (EtHN)<sub>4-b</sub>SiX<sub>b</sub> wherein b is from 1 to 2 inclusive;
- (EtMeN)<sub>4-b</sub>SiX<sub>b</sub> wherein b is from 1 to 2 inclusive;
- (Me<sub>2</sub>N)<sub>4-b</sub>SiX<sub>b</sub> wherein b is from 1 to 2 inclusive;
- (Et<sub>2</sub>N)<sub>4-b</sub>SiX<sub>b</sub> wherein b is from 1 to 2 inclusive;
- (Me<sub>2</sub>N)<sub>3-b</sub>(X)<sub>b</sub>Si-Si(X)<sub>b</sub>(NMe<sub>2</sub>)<sub>3-b</sub> wherein b is 1 or 2;
- (Et<sub>2</sub>N)<sub>3-b</sub>(X)<sub>b</sub>Si-Si(X)<sub>b</sub>(NEt<sub>2</sub>)<sub>3-b</sub> wherein b is 1 or 2;
- [(Me<sub>3</sub>Si)<sub>2</sub>N]<sub>4-b</sub>TiX<sub>b</sub> wherein b is 1 or 2, and X is Cl, Br, F or I;
- [(Me<sub>3</sub>Si)<sub>2</sub>N]<sub>5-b</sub>MX<sub>b</sub> wherein b is 2 or 3, X is Cl, Br, F or I, and M is Ta or Nb; and
- [(Me<sub>3</sub>Si)<sub>2</sub>N]<sub>6-b</sub>WX<sub>b</sub> wherein b is 1 or 2, and X is Cl, Br, F or I.

37. The metalorganic precursor of claim 32, wherein said precursor comprises silicon.

38. The metalorganic precursor of claim 32, wherein said precursor is selected from the group consisting of:

$[(\text{Me}_3\text{Si})_2\text{N}]_{4-b}\text{TiX}_b$  wherein b is 1 or 2, and X is Cl, Br or I;

$[(\text{Me}_3\text{Si})_2\text{N}]_{5-b}\text{MX}_b$  wherein b is 2 or 3, X is Cl, Br, F or I, and M is Ta or Nb;

$[(\text{Me}_3\text{Si})_2\text{N}]_{6-b}\text{WX}_b$  wherein b is 1 or 2, and X is Cl, Br, F or I.

39. A metalorganic precursor composition comprising a compound of formula (I):



wherein:

M is selected from the group of Ta, Ti, W, Nb, Si, Al and B;

a is a number equal to the valence of M;

$1 \leq b \leq (a-1)$ ;

$\text{R}_1$  and  $\text{R}_2$  can be the same as or different from one another, and are each independently selected from the group of H,  $\text{C}_1$ - $\text{C}_4$  alkyl,  $\text{C}_3$ - $\text{C}_6$  cycloalkyl, and  $\text{R}^0_3\text{Si}$ , where each  $\text{R}^0$  can be the same or different and each  $\text{R}^0$  is independently selected from H and  $\text{C}_1$ - $\text{C}_4$  alkyl; and

X is selected from the group of chlorine, fluorine, bromine and iodine.

40. The composition of claim 39, further comprising a silicon source reagent.

41. The composition of claim 40, wherein said silicon source reagent comprises a silane reagent selected from the group consisting of silane, alkylsilanes, halosilanes, and alkylhalosilanes, wherein alkyl is  $\text{C}_1$ - $\text{C}_4$  alkyl and halo is Cl, Br, F or I.

42. The composition of claim 39, further comprising an aluminum source reagent.

43. The composition of claim 42, wherein said aluminum source reagent comprises an alane reagent selected from the group consisting of alane, alkylalanes, haloalanes and alkylhaloalanes, wherein alkyl is  $\text{C}_1$ - $\text{C}_4$  alkyl and halo is Cl, Br, F or I.



44. The composition of claim 39, wherein said precursor comprises a compound selected from the group consisting of:

- (EtHN)<sub>6-b</sub>WX<sub>b</sub> wherein b is from 1 to 2 inclusive;
- (EtMeN)<sub>6-b</sub>WX<sub>b</sub> wherein b is from 1 to 2 inclusive;
- (Me<sub>2</sub>N)<sub>6-b</sub>WX<sub>b</sub> wherein b is from 1 to 2 inclusive;
- (Et<sub>2</sub>N)<sub>6-b</sub>WX<sub>b</sub> wherein b is from 1 to 2 inclusive;
- (EtHN)<sub>5-b</sub>MX<sub>b</sub> wherein M is Ta or Nb, and b is 1 or 2;
- (EtMeN)<sub>5-b</sub>MX<sub>b</sub> wherein M is Ta or Nb, and b is 1 or 2;
- (Me<sub>2</sub>N)<sub>5-b</sub>MX<sub>b</sub> wherein M is Ta or Nb, and b is 1 or 2;
- (Et<sub>2</sub>N)<sub>5-b</sub>MX<sub>b</sub> wherein M is Ta or Nb, and b is 1 or 2;
- (EtHN)<sub>4-b</sub>TiX<sub>b</sub> wherein b is from 1 to 2 inclusive;
- (EtMeN)<sub>4-b</sub>TiX<sub>b</sub> wherein b is from 1 to 2 inclusive;
- (Me<sub>2</sub>N)<sub>4-b</sub>TiX<sub>b</sub> wherein b is from 1 to 2 inclusive;
- (Et<sub>2</sub>N)<sub>4-b</sub>TiX<sub>b</sub> wherein b is from 1 to 2 inclusive;
- (EtHN)<sub>4-b</sub>SiX<sub>b</sub> wherein b is from 1 to 2 inclusive;
- (EtMeN)<sub>4-b</sub>SiX<sub>b</sub> wherein b is from 1 to 2 inclusive;
- (Me<sub>2</sub>N)<sub>4-b</sub>SiX<sub>b</sub> wherein b is from 1 to 2 inclusive;
- (Et<sub>2</sub>N)<sub>4-b</sub>SiX<sub>b</sub> wherein b is from 1 to 2 inclusive;
- (Me<sub>2</sub>N)<sub>3-b</sub>(X)<sub>b</sub>Si-Si(X)<sub>b</sub>(NMe<sub>2</sub>)<sub>3-b</sub> wherein b is 1 or 2;
- (Et<sub>2</sub>N)<sub>3-b</sub>(X)<sub>b</sub>Si-Si(X)<sub>b</sub>(NEt<sub>2</sub>)<sub>3-b</sub> wherein b is 1 or 2;
- [(Me<sub>3</sub>Si)<sub>2</sub>N]<sub>4-b</sub>TiX<sub>b</sub> wherein b is 1 or 2, and X is Cl, Br, F or I;
- [(Me<sub>3</sub>Si)<sub>2</sub>N]<sub>5-b</sub>MX<sub>b</sub> wherein b is 2 or 3, X is Cl, Br, F or I, and M is Ta or Nb; and
- [(Me<sub>3</sub>Si)<sub>2</sub>N]<sub>6-b</sub>WX<sub>b</sub> wherein b is 1 or 2, and X is Cl, Br, F or I.

45. The composition of claim 39, wherein said precursor comprises silicon.

46. The composition of claim 45, wherein said precursor comprises a compound selected from the group consisting of:

$[(\text{Me}_3\text{Si})_2\text{N}]_{4-b}\text{TiX}_b$  wherein b is 1 or 2, and X is Cl, Br, F or I;

$[(\text{Me}_3\text{Si})_2\text{N}]_{5-b}\text{MX}_b$  wherein b is 2 or 3, X is Cl, Br, F or I, and M is Ta or Nb; and

$[(\text{Me}_3\text{Si})_2\text{N}]_{6-b}\text{WX}_b$  wherein b is 1 or 2, and X is Cl, Br, F or I.

47. The composition of claim 39, further comprising a compound of formula (II):



wherein:

X is Cl or Br;

m, n and y can each be the same as or different from each other, and each is independently from 0 to 3 inclusive; and

R and R' are the same as or different from one another, and each is independently selected from the group of H, C<sub>1</sub>-C<sub>4</sub> alkyl, and C<sub>3</sub>-C<sub>6</sub> cycloalkyl.

48. The composition of claim 47, wherein said compound of formula (II) is selected from the group consisting of:

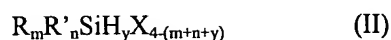
ClSiH<sub>3</sub>;

H<sub>2</sub>SiCl<sub>2</sub>;

Me<sub>3</sub>SiCl; and

t-Bu<sub>2</sub>SiCl<sub>2</sub>.

49. A method of forming Si<sub>3</sub>N<sub>4</sub> on a surface of a substrate by an ALCVD process, comprising functionalizing the surface with a nitrogen-containing functionality to form a functionalized surface, and contacting the functionalized surface with a silane halide compound under reaction conditions producing Si<sub>3</sub>N<sub>4</sub> as a reaction product on the surface of the substrate, wherein the silane halide has the formula (II):



wherein:

X is Cl or Br;

m, n and y can each be the same as or different from each other, and each is independently from 0 to 3 inclusive; and

R and R' are the same as or different from one another, and each is independently selected from the group of H, C<sub>1</sub>-C<sub>4</sub> alkyl, and C<sub>3</sub>-C<sub>6</sub> cycloalkyl.